UNIVERSITY OF PENNSYLVANIA

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AN ESSENTIAL PORTION OF

A DISSERTATION

IN CHEMICAL ENGINEERING

PRESENTED TO THE FACULTY OF THE GRADUATE SCHOOL IN

PARTIAL FULLFILMENT OF THE REQUIREMENTS FOR

THE DEGREE OF DOCTOR OF PHILOSOPHY

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Solubility and Density Isotherms for Sodium Sulfate–Ethylene Glycol–Water

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Solubilities and saturated solution densities are reported at intervals of 5° from 25° to 100° C. for sodium sulfate in aqueous ethylene glycol solutions. Only one liquid phase occurs regardless of glycol concentration. The lowering by the glycol of the sodium sulfate anhydrous-decahydrate transition temperature in saturated aqueous solutions was determined from 32.4° to just below 20° C. Over a wide intermediate range of water-glycol compositions the temperature-solubility curve of the anhydrous salt is almost invariant with temperature.

OWING to the inverted solubility relationship of anhydrous sodium sulfate in water, its commercial crystallization in most conventional evaporator-crystallizers is difficult. On evaporating a concentrated aqueous solution of sodium sulfate, a tenacious scale of the anhydrous salt tends to form on the heating surface.

To evaluate the technical feasibility of a new method being investigated by the authors to reduce or eliminate this difficulty, complete solubility data were needed for the system sodium sulfate–ethylene glycol–water. In essence the process involves maintaining ethylene glycol in a crystallizer used either to dehydrate Glauber's salt crystals or to evaporate an aqueous solution of the salt. The presence of glycol lowers and renders the solubility almost invariant with temperature. The crystallization process remains essentially one of evaporation.

The entire range of glycol concentration was investigated at temperatures from 25° to 100° C. Densities of saturated solutions and salt solubilities were determined over this range. With only traces of impurities present in the unpurified salt and glycol, it seemed possible that they would have a negligible effect on the solubility of sodium sulfate in aqueous glycol solutions. To establish the purity of materials required for reliable and reproducible results for this system, tests were run to compare the readily available salt and glycol with purified grades of both.

SOLUBILITIES

AQUEOUS GLYCOL SOLUTIONS. The solubility of Baker's C.P. anhydrous sodium sulfate in aqueous ethylene glycol solutions was determined at several temperatures for identical concentrations (31.4 weight % glycol in the solvent) of the technical and purified grades of ethylene glycol. The salt solubilities and saturated solution densities using these two grades of solvent were identical within the experimental error of check determinations. Both grades of solvent were adjusted to the desired compositions, utilizing the density-composition data of Spangler and Davies (*8*).

The technical grade of glycol, obtained from Carbide and Carbon Chemicals Corporation, was filtered before use for these determinations. Purified ethylene glycol was obtained by careful vacuum distillation of the technical grade under a pressure of 10 to 20 mm. of mercury.

The values of Spangler and Davies (*8*) at 25° C. for density, 1.1101 grams per ml., and for refractive index, 1.4300, for purified ethylene glycol are in agreement with the data obtained in this work.

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SODIUM SULFATE. The solubility in water of Baker's C.P. analyzed anhydrous sodium sulfate was determined over the temperature range of 25° C. to the boiling point. Saturated solution densities of these solutions were obtained up to 100° C. These values were compared with those obtained at several of the identical temperatures, using salt that had been purified by the method of Phipps and Reedy (*5*). This involved five recrystallizations of the Baker's C.P. salt from distilled water, operating between 5° and 30° C. to obtain the decahydrate salt. Recrystallizations at higher temperatures with the anhydrous salt as the crystalline form would not have been practical, owing to the relatively small change in solubility with temperature. The solubility and density data for these two grades of salt showed agreement within the limits of experimental precision.

Additional tests indicated that possible impurities contained in the C.P. salt had no detectable effect on the solubilities in the aqueous organic solutions.

As a result of these tests, Baker's C.P. anhydrous sodium sulfate was considered suitable for all other experiments in these studies.

PREPARATION OF SOLUTIONS. Water obtained from a laboratory Barnstead still was used throughout this work. Conductivity measurements on periodic samples of the distilled water were all of the order of 10^{-5} reciprocal ohm per centimeter.

TABLE I. ANALYTICAL DATA FOR SOLVENTS AND SATURATED SOLUTIONS (IN VACUO)

Solvent No.	Density of Solvent at 25° C., G./Ml.	Weight % Ethylene Glycol in Solvent	Weight % Na_2SO_4 in Satd. Soln. at 35° C.	Density of Soln. Satd. with Na_2SO_4 at 35° C., G./Ml.
H_2O	0.99704	0.0	32.98	1.3278
G-2[a]	0.99981	2.1	...	1.3143
G-6[a]	1.00444	5.8	...	1.2901
G-8	1.00716	8.0	27.69	1.2754
G-10[a]	1.00944	9.8	...	1.2649
G-12	1.01219	11.9	25.22	1.2522
G-14[a]	1.01500	14.0	...	1.2390
G-16	1.01730	15.7	22.59	1.2286
G-25	1.02916	24.4	16.84	1.1800
G-32	1.03847	31.4	12.85	1.1492
G-35[a]	1.04131	33.6	...	1.1411
G-40	1.04927	39.9	8.878	1.1223
G-44[a]	1.05559	44.9	...	1.1115
G-45	1.05637	45.5	6.813	1.1101
G-60	1.07392	60.6	3.251	1.0954
G-70	1.08456	69.8	1.898	1.0947
G-80	1.09349	78.8	1.122	1.0964
G-90	1.10340	90.3	0.699	1.1033
G-99	1.10960	99.2	0.487	1.1081

[a] Supplementary points for analytical curves (Figure 1).

Aqueous ethylene glycol solutions of approximately 8, 12, 16, 25, 32, 40, 45, 60, 70, 80, 90, and 99 weight % glycol were used as solvents in the region where anhydrous sodium sulfate was the stable solid phase. They were mixed to approximately the above values, with distilled water and technical grade glycol. The exact compositions are presented in Table I along with a few additional points, indicated by *a*, which were used in the construction of the analytical curves of Figure 1. The density and refractive index-composition data of Spangler and Davies (*8*) at 25.00° C. for aqueous ethylene glycol solutions were checked at several points by means of the purified glycol described above. They were found to be in excellent agreement. Accordingly, their smoothed

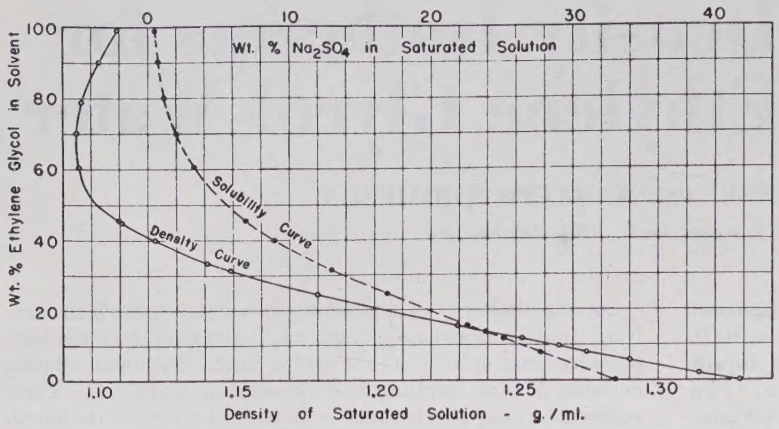
Wt. % Na_2SO_4 in Saturated Solution
Wt. % Ethylene Glycol in Solvent
Solubility Curve
Density Curve
Density of Saturated Solution - g./ml.

Figure 1. Plot for Determination of Ethylene Glycol–Water Compositions in Presence of Sodium Sulfate

The points shown represent experimentally determined salt solubility and saturated solution density values, all at 35.00° C.

values for density and refractive index were used to determine the composition of all salt-free aqueous glycol solutions encountered in this work. Densities were determined with a capped 10-ml. specific gravity bottle and refractive indices by an Abbe refractometer, both at 25.00° ± 0.01° C. Solvent compositions were determined to better than ±0.1 weight % glycol. The limiting factor here was the degree of precision of the available density and refractive index–composition data.

EXPERIMENTAL PROCEDURE

The constant temperature bath and much of the auxiliary equipment employed in this work have already been described (*9*, *10*). Although 2 to 3 hours was found to be more than sufficient for equilibration, a minimum of 5 hours was always allowed. The equilibrium time was again established by approaching the desired temperature from above and below. The methods used for this system required some modification because of the low volatility of the glycol, the occurrence of some hydration in the solid phase, and the somewhat higher temperatures involved.

Equilibrations. Carefully dried anhydrous sodium sulfate was slowly added to the solvent maintained above 35° C., at which temperature only the anhydrous salt occurs as the solid phase regardless of solvent composition. This procedure was required to prevent possible removal of water by the solid phase from the constant-composition solvents.

The only stable hydrate found over the range of temperatures and glycol concentrations covered was the decahydrate. In the relatively small region where this was encountered, complete analyses had to be run on liquid and solid phases at each experimental point. For these determinations the salt was added as described above. The temperature was then lowered slowly with vigorous agitation through the decahydrate-anhydrous transition point to the desired temperature. This procedure enabled the excess salt to pick up the water of hydration without caking. Seed crystals of the decahydrate were added periodically as the temperature was lowered to prevent the formation of a metastable solid phase. The heptahydrate, unstable in the presence of even small amounts of the decahydrate, was detected occasionally between 20° and 25° C. These studies were restricted to stable solid phases.

Salt Content. The weight per cent sodium sulfate in the saturated solutions was determined by evaporation to constant weight in 125-ml. glass-stoppered Erlenmeyer flasks in a vacuum oven. To determine the precision of such measurements, test runs were made in which various amounts and compositions of aqueous glycol solutions were successively added to and evaporated from given weights of salt. The salt content values are accurate to ±0.01 weight % salt for solutions containing more than 10% salt and somewhat better for smaller solubility values.

Density. The densities of the aqueous glycol solutions saturated with sodium sulfate were determined by a previously described technique (*9*) employing weighing pipets. Solutions involving solvents of about 80 weight % glycol or higher were sampled with a sintered glass filter connected to the tip of the pipet. The filter was required for these solutions since the dispersed salt did not settle to the bottom of the cell completely, even after much longer than the 15-minute settling time usually allowed. For solutions with lower glycol content the dispersed solid settled sufficiently in 15 minutes to give a clear supernatant solution. Identical results were obtained with these solutions whether the filter was used or not. The precision of these meas-

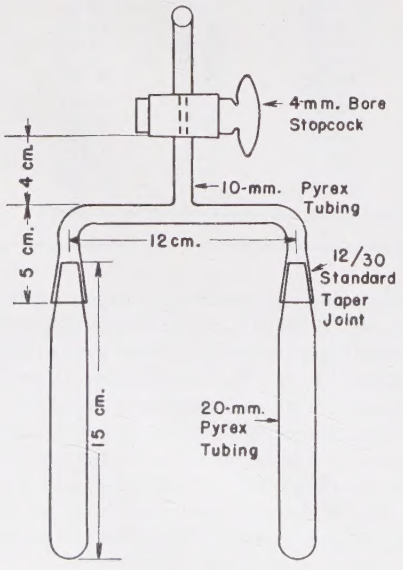

Figure 2. Vacuum Distillation Apparatus

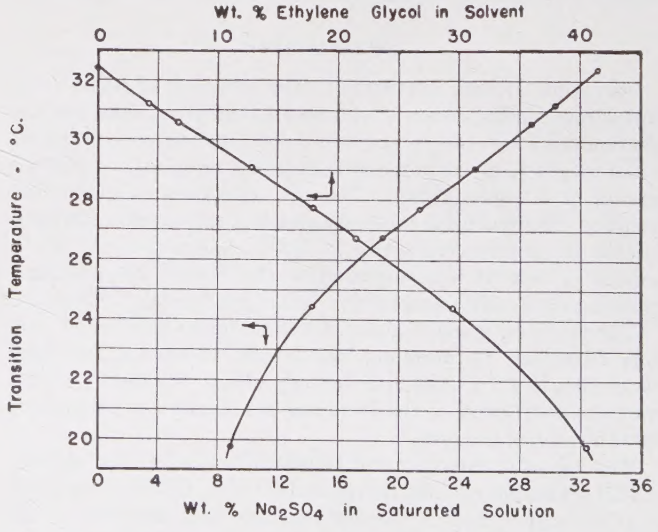

Figure 3. Variation of Na_2SO_4–$Na_2SO_4.10H_2O$ Transition Temperature with Aqueous Glycol Solvent Composition and Salt Content

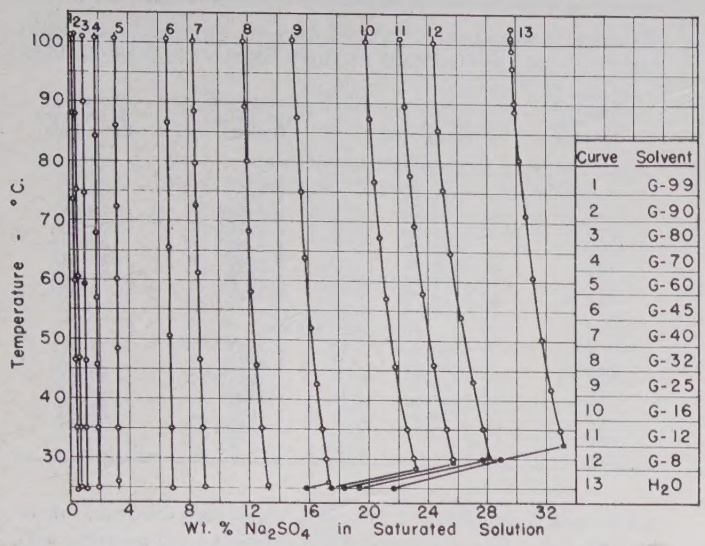

Figure 4. Solubility of Sodium Sulfate in Aqueous Ethylene Glycol Solutions

urements was about ±0.0003 gram per ml. However, at temperatures above 75° C. considerable difficulty was encountered in density determinations with solutions requiring the filter, owing to pronounced cooling of pipetted solutions during the prolonged sampling time.

Solid Phase Analysis. Two methods were used to determine the composition of the solid phase. The first, designated the "quick blot" test, was used to distinguish between the anhydrous salt and possible hydrates or solvates. For each sampling, several grams of the wet excess salt were removed, and the slurry was ejected on a filter paper in a Gooch crucible. The crucible was disconnected from the suction, inverted over filter paper, and blotted, and the weight loss determined. The entire procedure from the sampling to the capping of the weighing bottle required less than 10 seconds. Preliminary tests on anhydrous salt showed a weight loss of less than 1%, due to some adhering solution incompletely removed by the quick blot method. When applied to the decahydrate, the actual loss was slightly less than theoretical, indicating a small loss of hydration water. Nevertheless, the discrepancy between actual and theoretical values for these and other materials was considerably less than that resulting from commonly used alcohol and ether rinses of the wet crystals.

In the event that some hydration or solvation was indicated by this test, a more precise analysis was run on the solid phase using the wet residue method of Schreinemakers (*6*).

Analysis of Aqueous Glycol Solutions Containing Salt. The solutions in equilibrium with a hydrate as the solid phase required the determination of all three components in both phases at each experimental point. The sample for salt content was treated as usual. An inverted U-shaped glass tube was used to siphon out rapidly about 400 ml. of the supernatant saturated solution. This solution was then equilibrated with an excess of carefully dried anhydrous salt at 35.00° C., at which temperature the anhydrous salt was the stable solid phase regardless of glycol content. Salt content and saturated solution density values were obtained. From a carefully determined relationship of solvent composition to solubility and density at 35.00° C., the glycol content was readily and accurately obtained. These data are listed in Table I and plotted in Figure 1.

When the amount of available solution was too small for the preceding method of analysis, a vacuum distillation method was utilized. The distillation method was also used for the analyses of the wet solid phase from the Schreinemakers' wet-residue samples. It involved the quantitative separation of anhydrous salt and aqueous glycol solution. The sample was sealed in one leg of the unit shown in Figure 2. After the contents were frozen by surrounding this tube with a dry ice–acetone slurry, the unit was rapidly evacuated with a Hy-Vac pump. The stopcock was quickly closed and the slurry was placed about the distillate leg. The temperature of the leg containing the sample was increased slowly to room temperature. By carefully distilling to dryness, the salt content was readily obtained. Density or refractive index measurements on the distillate permitted the determination of the water-glycol ratio. These distillation units were connected to a manifold, and several analyses were carried out simultaneously.

For the wide range of salt and glycol contents encountered, the above methods were found to be more accurate and convenient than standard distillation methods, the Karl Fischer volumetric determination of water content (*2*), and organic oxidation techniques as applied to glycol (*3*, *4*).

Transition Points. The demarcation line between the regions of decahydrate and anhydrous sodium sulfate in equilibrium with aqueous glycol solutions was established from 32.4° (water as solvent) to 20° C (approximately 40% glycol). A "synthetic" method was considered more convenient and perhaps more accurate than "analytic" techniques for these determinations. The make-up of the cell solution was the same as described above. After an excess of 100 to 200 grams of salt had been added, the temperature of the outside bath was lowered slowly and regularly.

Three criteria were observed to indicate arrival at the transition point: (1) The solid phase was sampled and analyzed by the methods described above. (2) The solution was analyzed for salt content. (3) The rate of fall of the cell temperature with decrease of that of the outside bath was observed. When the transition point was reached, an increasing amount of hydrate water was found in the solid phase, and salt content of the solution decreased sharply. In addition, the temperature in the cell, while still falling very slowly, now lagged far behind that of the outside bath. When about half of the excess salt had been converted to

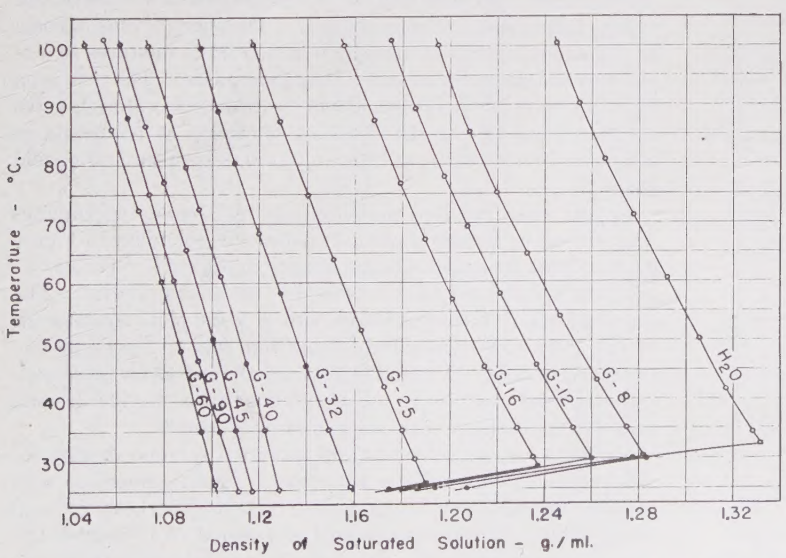

Figure 5. Density of Aqueous Ethylene Glycol Solutions Saturated with Sodium Sulfate

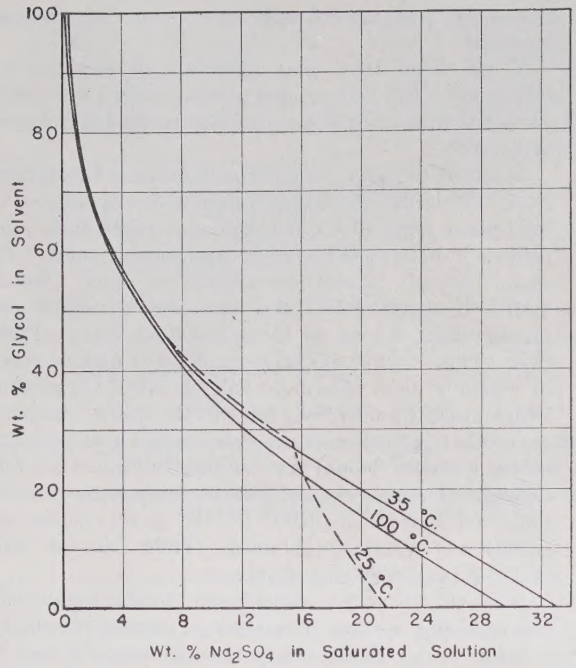

Figure 6. Composition Isotherms for Sodium Sulfate–Ethylene Glycol–Water

the hydrate, the outside bath was brought up to the temperature of the cell. After equilibrating for 24 hours, both phases were sampled and analyzed. Water or glycol was then added to the cell, but insufficient to convert the solid phase entirely to either the anhydrous or decahydrate form. After re-equilibrating at the same temperature, the two phases were again analyzed. The temperature involved was considered the transition point for that particular solvent only when the analysis of this solution proved to be identical with the preceding one in all three components. When the two sets of analyses differed beyond the limits of experimental error, the runs were repeated.

Solution densities and sodium sulfate solubilities are listed in Table II for aqueous ethylene glycol solutions in equilibrium with

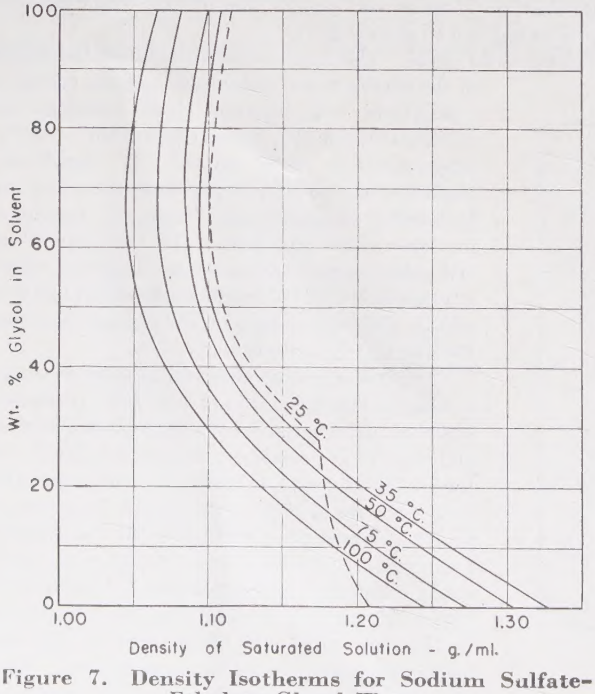

Figure 7. Density Isotherms for Sodium Sulfate–Ethylene Glycol–Water

TABLE II. AQUEOUS ETHYLENE GLYCOL SOLUTIONS IN EQUILIBRIUM WITH A SOLID PHASE OF BOTH Na_2SO_4 AND $Na_2SO_4.10H_2O$

Weight % Ethylene Glycol in Solvent	Transition Temp., ° C.	Density of Satd. Soln., G./Ml.	Weight % Na_2SO_4 in Satd. Soln.
	Experimental Points		
0.0	32.38	1.3324	33.27
4.3	31.20	1.3059	30.44
6.8	30.55	1.2903	28.88
12.9	29.08	1.2540	25.10
18.1	27.72	1.2236	21.48
21.6	26.74	1.2042	19.11
29.6	24.42	1.1672	14.38
40.6	19.78	1.1317	8.96
	Interpolated Values		
8.0	30.25	1.2827	28.15
11.9	29.32	1.2615	25.76
15.7	28.37	1.2381	23.20
24.4	25.94	1.1899	17.32
31.4	23.84	1.1607	13.40
39.9	20.18	1.1337	9.29

a solid phase consisting of mixtures of the anhydrous and decahydrate salt. The variation of the transition temperature with solvent composition and salt content is represented in Figure 3. The points shown represent experimental values. The interpolated values in Table II were obtained at solvent compositions corresponding to those of Table I from large scale plots similar to Figure 3.

ISOTHERMS

The density and solubility data were plotted on a scale large enough to permit values to be read within the precision of the experimental determinations. Curves were drawn through these points, and interpolated values were obtained at intervals of 5° from 25° to 100° C. These smoothed values for solubility and density isotherms are presented in Table III.

Experimental points for sodium sulfate solubility with aqueous glycol solvent composition as parameter are plotted against temperature in Figure 4. Similar plots for the density of the saturated solutions are presented in Figure 5. The exact solvent compositions corresponding to the various curves may be determined by reference to Table I. All open circles in these two plots are experimentally determined values involving a solid phase of the anhydrous salt. The solid points do not represent experimental values but were included because it was considered of interest to show the shape of the constant-solvent composition curves when extended into the hydrated solid-phase region. The values corresponding to the aqueous glycol solvents used for the constant-solvent composition runs in the anhydrous salt region were interpolated from large scale plots of the experimental solubility and density against solvent compositions. The sharp breaks in some of the curves represent transition points with mixtures of anhydrous and decahydrate salt as the solid phase. The points on these curves at temperatures above the transition values involve the anhydrous salt as the stable solid phase; at temperatures below the break points, sodium sulfate decahydrate is the solid phase.

Several isotherms are presented on rectangular coordinates with solvent composition plotted against salt solubility in Figure 6 and against saturated solution density in Figure 7. The 25° C. isotherm is indicated by a broken line for greater clarity. The sharp inflection in this curve on both of these plots corresponds to the anhydrous-decahydrate transition point. Isotherms between 35° and 100° C. would lie between the curves for these temperatures and would have the anhydrous salt as the stable solid phase in equilibrium with the saturated solutions.

The data for salt solubility and saturated solution density for the system sodium sulfate–water are in good agreement with those of various other investigators, including Berkeley (*1*) and others whose data are reproduced or referred to by Seidell (*7*). No previous work has been reported on the solubility of sodium sulfate in aqueous ethylene glycol solvents.

Table III. Smoothed Values for Solubility and Density Isotherms

(Solid phase is anhydrous sodium sulfate unless otherwise indicated)

Temp. ° C.	Wt. % Na_2SO_4 in Satd. Soln.	Density of Satd. Soln., G./Ml.	Wt. % Na_2SO_4 in Satd. Soln.	Density of Satd. Soln., G./Ml.
	DISTD. WATER AS SOLVENT		8 WT. % ETHYLENE GLYCOL IN SOLVENT	
25.00	21.74[a]	1.2075	19.36[a]	1.1918
30.00	29.10[a]	1.2834	27.70[a]	1.2780
35.00	32.98	1.3278	27.69	1.2754
40.00	32.50	1.3196	27.24	1.2673
45.00	32.08	1.3123	26.82	1.2592
50.00	31.72	1.3059	26.45	1.2520
55.00	31.46	1.2993	26.09	1.2453
60.00	31.20	1.2929	25.79	1.2390
65.00	30.97	1.2866	25.52	1.2326
70.00	30.71	1.2801	25.27	1.2264
75.00	30.47	1.2734	25.06	1.2203
80.00	30.24	1.2666	24.88	1.2141
85.00	30.02	1.2603	24.72	1.2084
90.00	29.86	1.2545	24.60	1.2033
95.00	29.73	1.2495	24.52	1.1991
100.00	29.65	1.2450	24.45	1.1953
	11.9 WT. % ETHYLENE GLYCOL IN SOLVENT		15.7 WT. % ETHYLENE GLYCOL IN SOLVENT	
25.00	18.37[a]	1.1858	17.46[a]	1.1808
30.00	25.69	1.2604	23.02	1.2357
35.00	25.22	1.2522	22.59	1.2286
40.00	24.76	1.2447	22.19	1.2219
45.00	24.40	1.2378	21.85	1.2155
50.00	24.08	1.2311	21.56	1.2093
55.00	23.79	1.2248	21.30	1.2034
60.00	23.53	1.2185	21.06	1.1975
65.00	23.30	1.2126	20.84	1.1919
70.00	23.08	1.2066	20.64	1.1864
75.00	22.90	1.2011	20.47	1.1808
80.00	22.74	1.1955	20.32	1.1753
85.00	22.59	1.1899	20.20	1.1700
90.00	22.45	1.1847	20.09	1.1651
95.00	22.32	1.1800	20.00	1.1603
100.00	22.21	1.1759	19.91	1.1556
	24.4 WT. % ETHYLENE GLYCOL IN SOLVENT		31.4 WT. % ETHYLENE GLYCOL IN SOLVENT	
25.00	15.82[a]	1.1748	13.28	1.1589
30.00	17.13	1.1855	13.05	1.1538
35.00	16.84	1.1800	12.85	1.1492
40.00	16.59	1.1744	12.67	1.1445
45.00	16.36	1.1691	12.51	1.1398
50.00	16.15	1.1642	12.37	1.1353
55.00	15.98	1.1594	12.25	1.1310
60.00	15.83	1.1546	12.15	1.1270
65.00	15.69	1.1500	12.08	1.1228
70.00	15.57	1.1453	12.02	1.1184
75.00	15.47	1.1406	11.96	1.1138
80.00	15.36	1.1355	11.90	1.1095
85.00	15.27	1.1305	11.84	1.1054
90.00	15.19	1.1258	11.79	1.1012
95.00	15.11	1.1214	11.73	1.0975
100.00	15.03	1.1172	11.67	1.0942
	39.9 WT. % ETHYLENE GLYCOL IN SOLVENT		45.5 WT. % ETHYLENE GLYCOL IN SOLVENT	
25.00	9.036	1.1289	6.924	1.1171
30.00	8.947	1.1256	6.865	1.1135
35.00	8.878	1.1223	6.813	1.1101
40.00	8.820	1.1189	6.770	1.1068
45.00	8.762	1.1154	6.736	1.1035
50.00	8.707	1.1119	6.709	1.1003
55.00	8.656	1.1084	6.689	1.0968
60.00	8.610	1.1049	6.670	1.0932
65.00	8.569	1.1009	6.653	1.0893
70.00	8.530	1.0966	6.637	1.0850
75.00	8.494	1.0920	6.621	1.0807
80.00	8.461	1.0877	6.606	1.0764
85.00	8.430	1.0837	6.593	1.0724
90.00	8.399	1.0798	6.579	1.0686
95.00	8.369	1.0761	6.564	1.0648
100.00	8.340	1.0724	6.549	1.0609
	60.6 WT. % ETHYLENE GLYCOL IN SOLVENT		69.8 WT. % ETHYLENE GLYCOL IN SOLVENT	
25.00	3.263	1.1021	1.922	1.1014
30.00	3.256	1.0985	1.910	1.0981
35.00	3.251	1.0954	1.898	1.0947
40.00	3.242	1.0922	1.885	1.0911
45.00	3.231	1.0889	1.873	1.0879
50.00	3.219	1.0857	1.862	1.0844
55.00	3.205	1.0823	1.851	1.0808
60.00	3.194	1.0786	1.841	1.0771
65.00	3.184	1.0748	1.831	1.0734
70.00	3.174	1.0707	1.821	1.0695
75.00	3.164	1.0664	1.811	1.0655
80.00	3.155	1.0621	1.799	1.0614
85.00	3.148	1.0580	1.788	1.0572
90.00	3.139	1.0542	1.779	1.0530
95.00	3.130	1.0504	1.768	1.0487
100.00	3.120	1.0464	1.755	1.0444

Temp., ° C.	Wt. % Na_2SO_4 in Satd. Soln.	Density of Satd. Soln., G./Ml.	Wt. % Na_2SO_4 in Satd. Soln.	Density of Satd. Soln., G./Ml.
	78.8 WT. % ETHYLENE GLYCOL IN SOLVENT		90.3 WT. % ETHYLENE GLYCOL IN SOLVENT	
25.00	1.143	1.1035	0.773	1.1113
30.00	1.133	1.0999	0.734	1.1071
35.00	1.122	1.0964	0.699	1.1033
40.00	1.111	1.0927	0.668	1.0994
45.00	1.098	1.0892	0.638	1.0954
50.00	1.085	1.0856	0.608	1.0916
55.00	1.072	1.0820	0.578	1.0877
60.00	1.059	1.0785	0.550	1.0839
65.00	1.045	1.0750	0.527	1.0804
70.00	1.032	1.0718	0.508	1.0769
75.00	1.018	1.0686	0.494	1.0733
80.00	1.005	....	0.481	....
85.00	0.991	....	0.469	....
90.00	0.977	....	0.457	....
95.00	0.964	....	0.447	....
100.00	0.950	....	0.438	....

Temp., ° C.	Wt. % Na_2SO_4 in Satd. Soln.	Density of Satd. Soln., G./Ml.	Temp., ° C.	Wt. % Na_2SO_4 in Satd. Soln.	Density of Satd. Soln. G./Ml.
	99.2 WEIGHT % ETHYLENE GLYCOL IN SOLVENT				
25.00	0.540	1.1146	65.00	0.329	1.0890
30.00	0.514	1.1113	70.00	0.309	1.0852
35.00	0.487	1.1081	75.00	0.292	1.0811
40.00	0.458	1.1052	80.00	0.276	....
45.00	0.430	1.1023	85.00	0.262	....
50.00	0.402	1.0995	90.00	0.249	....
55.00	0.376	1.0963	95.00	0.240	....
60.00	0.351	1.0927	100.00	0.230	....

[a] Solid phase, $Na_2SO_4.10H_2O$.

Table IV. Solubility Determinations at Elevated Temperatures

Temp., ° C.	Wt. % Na_2SO_4 in Satd. Soln.	Temp., ° C.	Wt. % Na_2SO_4 in Satd. Soln.	Temp., ° C.	Wt. % Na_2SO_4 in Satd. Soln.
WATER AS SOLVENT		41.0 WT. % GLYCOL AS SOLVENT		67.5 WT. % GLYCOL AS SOLVENT	
103.0[a]	....	107.1[a]	...	114.4[a]	...
102.60	29.622	106.65	7.915	113.85	1.975
101.05	29.631	104.50	7.913	112.50	1.986
100.46	29.638	105.60	7.910	109.80	1.997
98.85	29.663	103.50	7.911	106.50	2.003
96.10	29.724	100.00	7.914	98.75	2.034
10.5 WT. % GLYCOL AS SOLVENT		45.5 WT. % GLYCOL AS SOLVENT		75.5 WT. % GLYCOL AS SOLVENT	
104.5[a]	....	108.3[a]	...	119.7[a]	...
104.30	22.913	108.00	6.624	119.15	1.104
103.50	22.915	106.60	6.611	118.25	1.108
102.80	22.922	105.05	6.609	115.80	1.120
99.75	22.952	100.35	6.644	112.70	1.132
18.1 WT. % GLYCOL AS SOLVENT		48.6 WT. % GLYCOL AS SOLVENT		108.40	1.138
104.9[a]	....	108.9[a]	...	103.40	1.168
104.50	18.457	108.80	5.528	100.00	1.190
102.93	18.462	106.30	5.530	80.0 WT. % GLYCOL AS SOLVENT	
100.40	18.477	103.15	5.545	124.3[a]	...
96.40	18.516	98.75	5.554	123.45	0.795
24.2 WT. % GLYCOL AS SOLVENT		60.1 WT. % GLYCOL AS SOLVENT		121.50	0.792
105.1[a]	....	111.3[a]	...	117.25	0.791
104.80	15.189	110.95	3.188	107.20	0.840
103.90	15.192	110.13	3.187	99.30	0.860
103.05	15.201	108.95	3.183	90.0 WT. % GLYCOL AS SOLVENT	
99.65	15.228	108.10	3.184	136.3[a]	...
36.2 WT. % GLYCOL AS SOLVENT		100.00	3.201	135.05	0.421
106.0[a]	....			131.20	0.413
105.75	9.839			128.30	0.407
104.40	9.836			126.30	0.408
103.00	9.840			122.70	0.414
101.75	9.859			100.00	0.454

[a] Approximate boiling point.

Figure 4 shows that the temperature-solubility curves become almost vertical over the whole range of 25° to 100° C. for solvents of a large intermediate range of water-glycol ratios. On in-

creasing the glycol content above about 50%, the decrease in solubility with temperature increase tends to become a little larger even though the actual solubility value is decreasing.

A large number of aqueous glycol solvents was employed in order to establish definitely whether there is a reversal of the slopes of the inverted solubility curves. The decrease in solubility with increase in temperature over a wide middle portion of the solvent composition range may be small enough to reduce appreciably the crystalline deposit on the heating element of an evaporator-crystallizer.

An inflection point is known to occur at about 125° C. for the solubility curve of the anhydrous salt in water. Since this temperature would undoubtedly be different for the various glycol concentrations, an attempt was made to ascertain whether this inflection point was attainable for any of the solvents at atmospheric pressure. Accordingly, some additional solubility determinations were run above 100° C. with solvents ranging from 0 to 90 weight % glycol. These results are listed in Table IV. A precision of considerably better than ±0.01 weight % salt was required. At given solvent compositions the temperature was lowered from close to the boiling point to a series of equilibrium temperatures at intervals of a few degrees. Tests indicated no appreciable change in solvent composition during the course of any of these runs.

The data of Table IV show an apparent inflection point below the atmospheric boiling point for many of the aqueous glycol solvents. These are not considered conclusive, however, because of the difficulties of sampling at these temperatures and the very small changes in solubility over the temperature increments involved. Nevertheless, they seem to indicate that an extension of the curves of Figure 4 to the boiling points of the solution would find them practically vertical for solutions with 40 weight % or higher glycol as solvent. The approximate boiling points included in Table IV are intended to indicate the degree to which these limiting temperatures were approached.

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